

A soft ellipsoid potential for biaxial molecules : Modeling and computer simulation

Jayashree Saha

Department of Physics, University of Calcutta

92, A.P.C. Road, Kolkata - 700009, India

E-mail : jsphy@caluniv.ac.in

June 25, 2015

Abstract

A soft ellipsoid contact potential model for a pair of biaxial ellipsoidal molecules is proposed which considers the configuration dependent energy anisotropy explicitly along with their geometrical aspects. We performed Molecular Dynamics simulation study to generate both biaxial smectic and nematic phases using this new potential.

Liquid crystal forming compounds are complex organic molecules, having in general, cylindrically symmetric rod-like or disc-like structures,. Theoretical models, developed to study phase transitions, structures and dynamics of these systems, essentially strive to relate important molecular interactions to the experimentally observed phase behaviour and properties. In this respect, computer simulation is one of the most efficient methods which considers detailed microscopic interactions theoretically to explain and analyze macroscopic experimental observations. Non-polar liquid crystal molecules interact both through short-range hard interactions and long range attractive interactions originated primarily from electrostatic interactions [1]. To study a liquid crystal system using computer simulation two major steps are to be followed. The first one is the modelling of a suitable potential which takes into account the basic electrostatic interactions responsible for the generation of one (or more) specific phase(s) and the second step is to use an appropriate simulation method. These models may be broadly classified as full atomic, united atom, site-site and single site interaction models. The first three class of models are not computationally efficient as there are multi-site interaction terms present in the potential. The fourth type of model potentials can be used efficiently for computer simulation studies of these complex molecular systems in a realistic way.

Single-site potentials require determination of σ , distance of closest approach as a function of orientation and center of mass distance for a pair of molecules and it is a difficult task to estimate this correctly in case of anisotropic molecular systems like liquid crystals. Additionally, the potentials must capture both the geometric and energy anisotropies of the systems consistently. To develop single-site model potentials which are accurate, relatively simple and computationally efficient, a rod-like rigid molecule may be approximated as a prolate ellipsoid. The main idea behind it is the representation of the interactions between a pair of liquid crystal molecules by their joint probability, where each molecule has Gaussian charge distribution centred around the molecular centroids. Corner [2] developed a model potential based on this idea which makes the analytical calculations remarkably simplified. Further significant development of this class of potential was done by Berne’s group which led to widely used Gay-Berne(G-B) potential [3]. These models were basically modified form of Lennard-Jones potential where the energy strength parameter ϵ and energy range parameter σ depended on molecular orientations and positions. In this form it provided both attractive and repulsive contributions of the intermolecular interactions of rigid, uniaxial molecules, in a computationally tractable way. These potentials known as Gaussian overlap potentials (GOP) have become popular in simulation studies due to their comparatively simplified approach in determining the energy contribution of a pair of ellipsoidal molecules. However, the G-B potential in its original form being generally restricted to uniaxial molecules is not an effective model when the multiplicity of phases adopted by liquid crystal molecules are to be studied. Modifications [4] and some parametrizations [5] of Gay-Berne potential have been proposed in order to study the behaviour of biaxial phases but these GOP models are not in conformity with the actual geometry of the molecule. The range function and the energy strength function in these potentials do not correctly estimate the interactions between the non-uniaxial ellipsoidal particles. Most of the real liquid crystal molecules do not have cylindrical uniaxial structures, therefore, biaxial contribution

to the potential is essential when one studies various phase structures adopted by the real molecules. Though much progress in the experimental study have been achieved, there has been comparatively little theoretical work done on this important class of liquid crystal forming molecules which have biaxial structures.

Perram-Wertheim [6] ellipsoid contact potential (ECP) had advantages over Gaussian overlap type potential because the ECP calculated geometrical contact point accurately for ellipsoidal structures including biaxial molecules. ECP represented the ellipsoids as quadratic forms to solve the contact function accurately by doing an optimization calculation. Despite this fact, ECP has not yet been widely used to study liquid crystals because it did not differentiate in energies due to different molecular configurations, thereby neglecting the proper weightage of the energy strength contribution to the potential. Energy strength parameter ϵ was taken as a constant in the ECP therefore well depth in this attractive-repulsive potential did not show correct behaviour. In our earlier work [8], we modelled a soft ellipsoid contact potential for uniaxial ellipsoidal molecules, considering the configuration dependent energy anisotropy along with their geometrical aspects. In this paper we generalize the earlier model by including biaxial contribution in the pair interaction potential for ellipsoidal molecules. Explicit analytical expressions for proper range and strength parameters alongwith related forces and torques are also provided. In addition, the molecular dynamics simulation study shows that this new soft ellipsoidal pair potential for biaxial molecules is suitable for generating both biaxial and uniaxial liquid crystal phases successfully in a single component rod-like molecular system.

In our model the charge distribution of molecules are described as ellipsoidal and are approximately represented by 3-D gaussian functions, i.e. the density of the centre of force along the axis of a molecule is a Gaussian function of distance from the center of the ellipsoid. The total interaction of two molecules is again a Gaussian distribution and is a function of their intercenter distance and relative orientations.

The pair interaction potential of two ellipsoidal molecules can be evaluated from the joint probability distribution of two Gaussians following convolution integral principle. This joint distribution function is proportional to

$$\exp[\mathbf{r}^T \cdot \mathbf{H}^{-1} \cdot \mathbf{r}]$$

where \mathbf{r} is the intermolecular vector connecting the centers of the ellipsoids and the matrix \mathbf{H} depends on the axes lengths and the relative orientations of three principal semi-axes of the two interacting ellipsoids. Both the energy range function σ i.e. the permitted closest distance between molecular pairs and the energy strength function ϵ which gives estimation of potential depths and widths, depend on this form of joint probability distribution functions.

The model pair potential which is a modified version of Lennard-Jones type interaction potential for the prolate ellipsoidal molecules can be represented in a shifted form as

$$U = 4\epsilon(\hat{\alpha}, \hat{\beta}, \hat{r}) \left[\left(\frac{\sigma_0}{r - \sigma(\hat{\alpha}, \hat{\beta}, \hat{r}) + \sigma_0} \right)^{12} - \left(\frac{\sigma_0}{r - \sigma(\hat{\alpha}, \hat{\beta}, \hat{r}) + \sigma_0} \right)^6 \right]. \quad (1)$$

where, $\hat{\alpha}$ and $\hat{\beta}$, are the orthogonal rotation matrices for transformation from space-fixed to molecule fixed coordinates for molecules 1 and 2 respectively and the value of σ_0 is equal to the smallest semi-axis length of the ellipsoid.

Unlike constant ϵ parameter in ECP model, our model considers relative configuration dependent ϵ for a molecule pair because they are characterised by highly non-spherical charge distributions. The energy strength function ϵ in our model potential is taken as

$$\epsilon = \epsilon_0 \epsilon_1^\nu(\hat{\alpha}, \hat{\beta}) \epsilon_2^\mu(\hat{\alpha}, \hat{\beta}, \hat{r}). \quad (2)$$

Here, ϵ_0 is a constant term and μ, ν are adjusting parameters for relative well depth variation in different compounds; ϵ_1 is a function of $\hat{\alpha}$ and $\hat{\beta}$; ϵ_2 depends additionally on \hat{r} , which is the unit vector along the intermolecular vector connecting the centers of the ellipsoids.

To calculate ϵ_2 , we consider diagonal energy matrix for a biaxial molecule as

$$\gamma = \begin{pmatrix} (\frac{\epsilon_0}{\epsilon_x})^{\frac{1}{\mu}} & 0 & 0 \\ 0 & (\frac{\epsilon_0}{\epsilon_y})^{\frac{1}{\mu}} & 0 \\ 0 & 0 & (\frac{\epsilon_0}{\epsilon_z})^{\frac{1}{\mu}} \end{pmatrix}. \quad (3)$$

where $\epsilon_x, \epsilon_y, \epsilon_z$ are equal to the well depths for side by side (s-s), width to width (w-w) and end to end (e-e) configurations and for the biaxial model we take $\epsilon_x > \epsilon_y > \epsilon_z$. We also take $\epsilon_0 = \epsilon_x$.

Defining matrices **A** and **B** which correspond to the first and second molecule respectively as

$$\mathbf{A} = \hat{\alpha}^\top \gamma \hat{\alpha}; \quad \mathbf{B} = \hat{\beta}^\top \gamma \hat{\beta}. \quad (4)$$

We write

$$\mathbf{H_E} = \lambda_E \mathbf{A} + (1 - \lambda_E) \mathbf{B}. \quad (5)$$

where λ_E is an energy related adjustable parameter such that $\lambda_E \in [0, 1]$ and this makes the object function

$$S_E(\lambda_E) = \lambda_E (1 - \lambda_E) \hat{r}^\top \cdot \mathbf{H_E}^{-1} \cdot \hat{r}. \quad (6)$$

an optimum. This object function gives correct estimation of the energy strength function by properly incorporating asymmetric configurations of a biaxial molecule pair.

The \hat{r} dependent part of the energy strength function ϵ_2 in our model potential is taken as

$$\begin{aligned} \epsilon_2(\hat{\alpha}, \hat{\beta}, \hat{r}) &= \lambda_E (1 - \lambda_E) \hat{r}^\top \cdot [(\lambda_E \mathbf{A} + (1 - \lambda_E) \mathbf{B})^{-1} \cdot \hat{r} \\ &= \lambda_E (1 - \lambda_E) \hat{r}^\top \cdot \mathbf{H_E}^{-1} \cdot \hat{r} \end{aligned} \quad (7)$$

We take ϵ_1 for biaxial molecules as [7]

$$\epsilon_1(\hat{\alpha}, \hat{\beta}) = \sigma_t |\mathbf{H}'_{\mathbf{E}}|^{-1/2}. \quad (8)$$

where $\mathbf{H}'_{\mathbf{E}} = \frac{1}{2}(\mathbf{A} + \mathbf{B})$ and $\sigma_t = \sqrt{2\frac{\sigma_y}{\sigma_x}\sigma_0^3[(\frac{\sigma_y}{\sigma_x}) + (\frac{\sigma_z}{\sigma_x})^2]}$; σ_x , σ_y and σ_z are the values of the range function for s-s, w-w and e-e configurations respectively. We calculate σ following ECP [6].

Defining matrices \mathbf{M} and \mathbf{N} related to the first and the second molecule respectively as

$$\mathbf{M} = \hat{\alpha}^T \mathbf{S}^2 \hat{\alpha}; \quad \mathbf{N} = \hat{\beta}^T \mathbf{S}^2 \hat{\beta} \quad (9)$$

where diagonal shape matrix \mathbf{S} takes the following form

$$\mathbf{S} = \begin{pmatrix} \sigma_x & 0 & 0 \\ 0 & \sigma_y & 0 \\ 0 & 0 & \sigma_z \end{pmatrix}. \quad (10)$$

and $\mathbf{H}_{\mathbf{D}} = \lambda_D \mathbf{M} + (1 - \lambda_D) \mathbf{N}$. We express the distance of closest approach for biaxial molecules σ in the following form

$$\sigma^{-2} = \lambda_D(1 - \lambda_D)(\hat{r}^T \cdot \mathbf{H}_{\mathbf{D}}^{-1} \cdot \hat{r}). \quad (11)$$

where λ_D is the shape related adjustable parameter. For our biaxial model $\sigma_x < \sigma_y < \sigma_z$. The potential is not isotropic at large distance which gives small thermodynamic contribution and therefore neglected for simplicity. The forces and torques are derived analytically for the biaxial ellipsoid. The expressions for force \vec{f} and torque $\vec{\tau}$ are

$$\begin{aligned} \vec{f} = \frac{8\epsilon_0\epsilon_1^\nu\epsilon_2^\mu}{\sigma_0 r^2} [& (3r^2(2\rho^{-13} - \rho^{-7})\hat{r} + 3\sigma^3\lambda_D(1 - \lambda_D) \\ & (2\rho^{-13} - \rho^{-7})\{\mathbf{k} - (\hat{r} \cdot \mathbf{k})\hat{r}\} - \lambda_E(1 - \lambda_E) \\ & \mu\epsilon_2^{-1}\sigma_0(\rho^{-12} - \rho^{-6})\{\mathbf{k}_E - (\hat{r} \cdot \mathbf{k}_E)\hat{r}\}) \\ & . \end{aligned} \quad (12)$$

$$\begin{aligned} \vec{\tau}_{1st \text{ mol.}} = \frac{8\epsilon_0\epsilon_1^\nu\epsilon_2^\mu}{r^2} [& -3\sigma^3\lambda_D^2(1 - \lambda_D)(\mathbf{k} \cdot \mathbf{M} \times \mathbf{k}) \\ & (2\rho^{-13} - \rho^{-7})/\sigma_0 + \lambda_E^2(1 - \lambda_E)(\mathbf{k}_E \cdot \mathbf{A} \times \mathbf{k}_E) \\ & (\rho^{-12} - \rho^{-6})] + \nu U \epsilon : \mathbf{E}^{-1} \mathbf{M} \\ & . \end{aligned} \quad (13)$$

(ϵ in equation (12) is the Levi-Civita tensor)

To check the suitability of the proposed model, we performed a sample NVE Molecular Dynamics (MD) simulation considering a system of prolate biaxial ellipsoids, interacting through the model potential described in the previous section. In this simulation we take two systems having different aspect ratios and well depth ratios. The systems consisting of 1372 ellipsoids interacting through this new potential all have $\mu = 1, \nu = 2$. The other set of parameters are taken as follows:

The ratios $\sigma_x : \sigma_y : \sigma_z$ have values 1 : 1.5 : 4.5 and 1 : 2 : 4.5 and corresponding $I_{xx}^*, I_{yy}^*, I_{zz}^*$ have the set of values (1.125, 1.062, 0.16); (1.2125, 1.062, 0.25) for two systems respectively. All the systems have $\epsilon_x/\epsilon_z = 1/30$ but having different ϵ_y/ϵ_z values 1/7, 1/8.5 for two systems respectively.

In the NVE MD simulation, 1372 molecules were confined in the cubic box obeying minimum image convention. The run started from a density $\rho^* = \rho\sigma_0^3 = 0.01$ with ellipsoidal molecules loaded on the sites of FCC lattice and having parallel orientation. For MD initial step translational and angular velocities were assigned from the Gaussian distribution of velocities at a higher temperature. This structure was not a stable structure at this density and it was melted at a reduced temperature $T^* = k_B T/\epsilon_0 = 4.0$. We used this isotropic configuration which was both orientationally and translationally disordered, as the initial configuration. Forces and torques were calculated from equations (12) and (13) using leap-frog algorithm [9]. To get the most ordered structure for the system, we increased the density from $\rho^* = 0.01$ to the desired values of $\rho^* = 0.19$ and 0.16 respectively for two set of systems with an increment size of 0.001 upto $\rho^* = 0.1$ and 0.01 for the rest. Temperature was then lowered in steps to help the molecules set with more order. The systems were cooled down to a very low reduced temperature $T^* = k_B T/\epsilon_0 = 0.4$. The interaction potential was taken equal to half the simulation box length. The time step size $\delta t^* = \delta t/(m\sigma_0^2/\epsilon_0)^{1/2} = 0.0012$ during cooling process. The orientations of molecules were described by quaternions instead of Eulerian angles to get the singularity-free orientational equations of motion.

To investigate the phase behaviour we started increasing the temperature T^* gradually. For each temperature we calculated the orientational order parameters, correlation functions to identify the particular liquid crystal phase. To achieve an equilibrated higher temperature configuration from more ordered low temperature phase 2×10^5 cycles were required far from transition and 5×10^5 near transition.

The orientational order parameter for uniaxial phase was calculated from the largest eigen value obtained by diagonalization of the order parameter tensor

$$Q_{\alpha\beta} = \frac{1}{2N} \sum (3e_{i\alpha}e_{i\beta} - \delta_{\alpha\beta}) \quad \alpha, \beta = x, y, z. \quad (14)$$

where $e_{i\alpha}$ was the α th component of the unit vector e_i along the symmetry axis of the i th molecule. Corresponding eigenvector gave the director which defines the average direction of molecular alignment.

The biaxial order parameter is $\langle R_{2,2}^2 \rangle = \langle \frac{1}{2}(1 + \cos^2 \beta) \cos 2\alpha \cos 2\gamma - \cos \beta \sin 2\alpha \sin 2\gamma \rangle$.

Additionally, to detect phase behaviour more accurately, some structural quantities were calculated. Those were radial distribution function $g(r) = \langle \delta(r - r_{ij}) \rangle_{ij} / 4\pi r^2 \rho$; density along the director $g(z) = \langle \delta(z - z_{ij}) \rangle_{ij} / \pi R^2 \rho$, where $z_{ij} = r_{ij} \cos \beta_{r_{ij}}$ was measured in the director frame and R is the radius of the cylindrical sampling region.

The snapshots of the simulation study show various phases formed at different temperatures. At $T^* = 0.4$ the smectic phase shows biaxiality in both cases as seen in the structures for the first system in Fig.1 and Fig.2 and for the second system in Fig.3 and Fig.4. At $T^* = 1.0$ it shows biaxial nematic phases in Fig.5 and Fig.6 for the first system and fig.7 and Fig.8 for the second system.

At $T^* > 5.0$ the system becomes isotropic. The radial distribution functions $g(r)$ (Fig.9, Fig.11) and density projection to the director $g(z)$ (Fig.10, Fig.12) are plotted at different temperatures for both systems. The values of orientational order parameters η and R_{22} are plotted in Fig.13 and Fig.14. Our results show that the new model potential can successfully reproduce both biaxial smectic and biaxial nematic phases. To demonstrate this new model's ability to generate biaxial liquid crystal phases we are reporting here some preliminary results. We plan to communicate details of phase transitional behaviour of this system in future work.

Liquid crystals show a rich multiplicity of phases which comes from their complex molecular structures giving rise to complex electromagnetic interactions. Other molecules of biological importance e.g. base pairs of DNA, lipids etc. basically have anisotropic biaxial structures. It is a difficult task to obtain the distance of closest approach as a function of orientation for these molecules. Additionally, this potential must capture the energetic strength anisotropy in a consistent way. GOP is a widely used model potential for the description of anisotropic behaviour of liquid crystals, however, it does not give a proper geometric interpretation. It can calculate the proper range and strength parameters for some specific configurations of identical uniaxial molecules. Perram and Wertheim took a different approach by introducing the ellipsoid contact function which took care of its true geometrical aspect by doing correct estimation of position of contact. Although applicable to any mixture in geometrical context it did not distinguish in energy functions between different relative orientations and positions of the non-spherical molecular pair. As this energy function is the basis of well depth estimation, it provides necessary and sufficient weightage while determining proper magnitude of the attractive part of the pair potential and thus acts as the most important contributor in fine tuning of the potential so that it generates a specific phase structure. In this work, considering molecular orientations and positions explicitly in both structural and energy strength related terms, we modelled a generalized pair potential for biaxial molecules. We further studied liquid crystal phases by doing molecular dynamics simulation utilizing this model potential. Though biaxial phases have been synthesized and analysed recently, theoretical studies including simulations have been done for more than three decades to understand the molecular properties needed for stabilization of these amazing phases. However, underlying intermolecular interactions responsible for the generation of these phases are still not understood properly and the present model potential will be able to provide essential information about the characteristic of single component rod-like molecular system crucial for obtaining biaxial phases. The simulation results show that this new model potential reported in this paper is qualitatively suitable to reproduce complex mesogenic behaviour of organic biaxial molecules in a realistic way. This new potential has been generalized to study systems comprising of multicomponent dissimilar molecules, results of which will be communicated in future publication.

The graphics software QMGA [10] was used for producing snapshots of the phases. This work was supported by UGC-UPE scheme of the University of Calcutta.

References

- [1] The molecular physics of liquid crystals, G. R. Luckhurst and G. W. Gray (eds), Academic Press Inc (December 1979).
- [2] J. Corner, Proc. R. Soc. London, Ser. A 192, 275 (1948).
- [3] J.G.Gay, B.J.Berne, J.Chem.Phys., **74**, 3316 (1981).
- [4] D. J. Cleaver, C. M. Care, M. P. Allen, and M. P. Neal, *Phys.Rev.E* **54** (1996) 559.
- [5] R.Berardi, L.Muccioli, S.Orlandi, M.Ricci, C.Zannoni, J. Phys.: Condens. Matter, **20**, 463101, 1-16 (2008).
- [6] J.W.Perram, M.S.Wertheim, J.L.Lebowitz, G.O.Willams, Chem.Phys.Letts., **105** (1984) 277-280.
- [7] R.Berardi, C.Fava, C.Zannoni, Chem.Phys.Lett., **236**, 462 (1995).
- [8] J.Saha, Phys. Letts. A, 375, 18, 1893, 2011.
- [9] Allen,M.P.; Tildesley,D.J. *Computer Simulation of Liquids* **1987**, Clarendon Press, Oxford.
- [10] A.T. Gabriel, T. Meyer, G. Germano, Visualization of molecules as convex bodies, *J. Chem. Th. Comput.*, **4** (2008) 468.

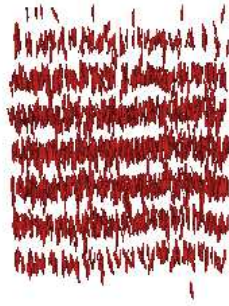


Figure 1: Snapshot at $T^* = 0.4$ for $\sigma_x : \sigma_y : \sigma_z = 1 : 1.5 : 4.5$

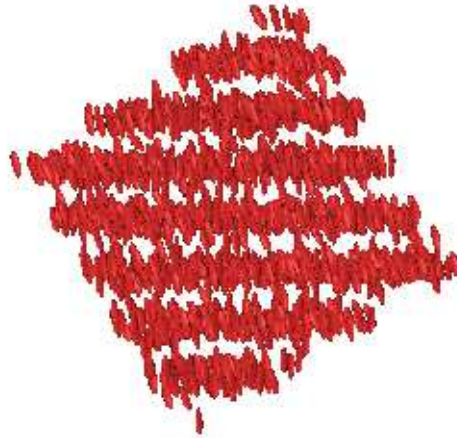


Figure 2: Snapshot (rotated) at $T^* = 0.4$ for $\sigma_x : \sigma_y : \sigma_z = 1 : 1.5 : 4.5$

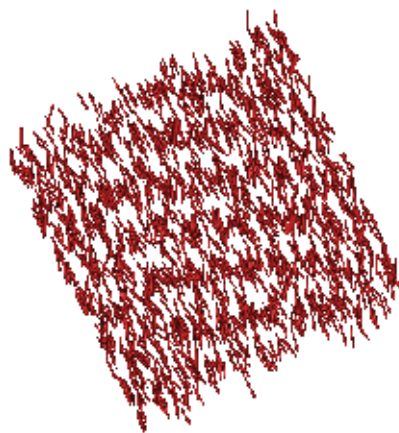


Figure 3: Snapshot at $T^* = 0.4$ for $\sigma_x : \sigma_y : \sigma_z = 1 : 2.0 : 4.5$

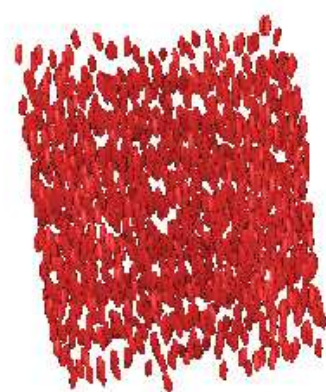


Figure 4: Snapshot (rotated) at $T^* = 0.4$ for $\sigma_x : \sigma_y : \sigma_z = 1 : 2.0 : 4.5$

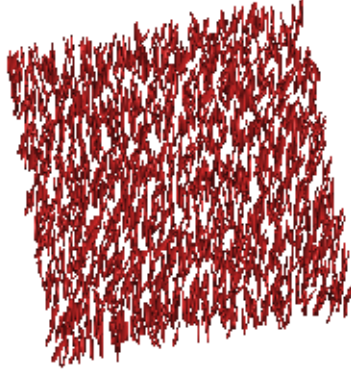


Figure 5: Snapshot at $T^* = 1.0$ for $\sigma_x : \sigma_y : \sigma_z = 1 : 1.5 : 4.5$

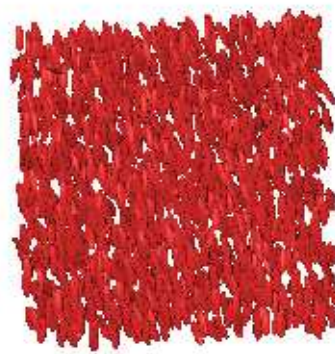


Figure 6: Snapshot (rotated) at $T^* = 1.0$ for $\sigma_x : \sigma_y : \sigma_z = 1 : 1.5 : 4.5$

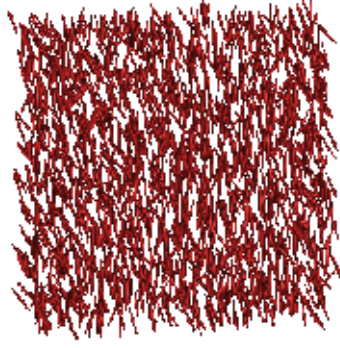


Figure 7: Snapshot (rotated) at $T^* = 1.0$ for $\sigma_x : \sigma_y : \sigma_z = 1 : 2.0 : 4.5$

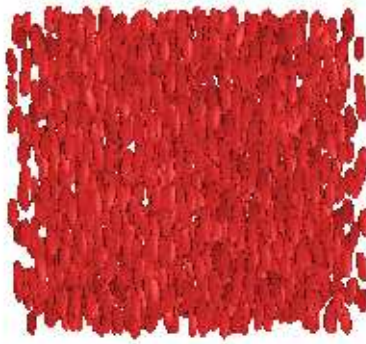


Figure 8: Snapshot (rotated) at $T^* = 1.0$ for $\sigma_x : \sigma_y : \sigma_z = 1 : 2.0 : 4.5$

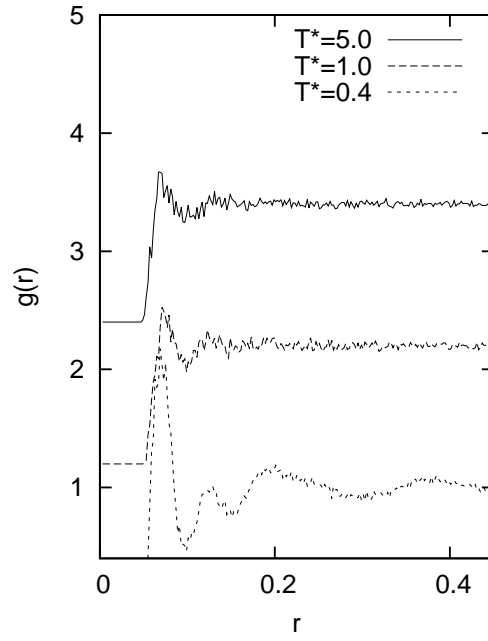


Figure 9: Radial distribution function $g(r)$ for $\sigma_x : \sigma_y : \sigma_z = 1 : 1.5 : 4.5$

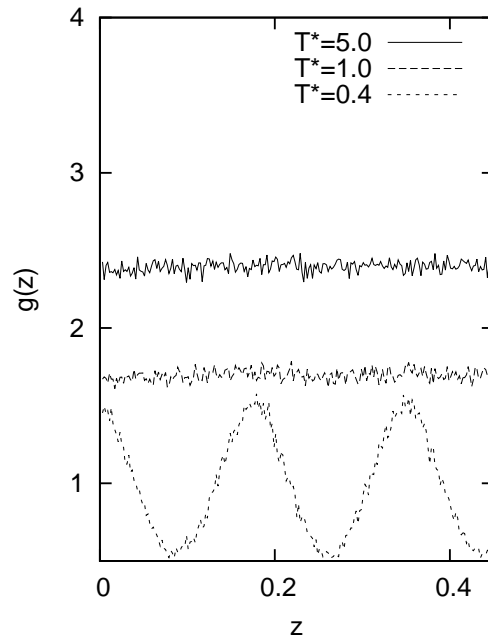


Figure 10: Density projection with respect to the director $g(z)$ for $\sigma_x : \sigma_y : \sigma_z = 1 : 1.5 : 4.5$

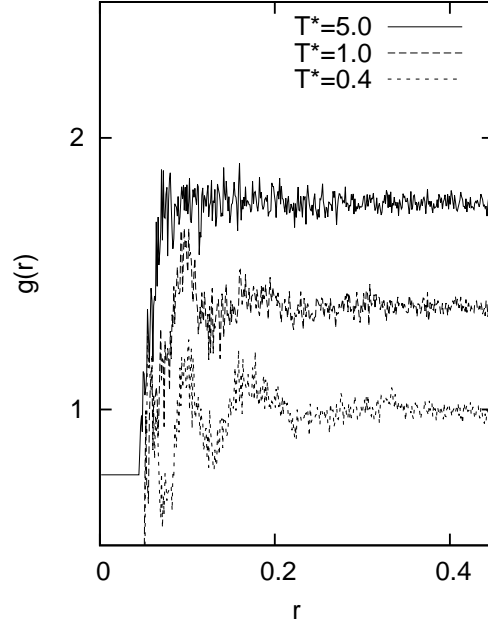


Figure 11: Radial distribution function $g(r)$ for $\sigma_x : \sigma_y : \sigma_z = 1 : 2 : 4.5$

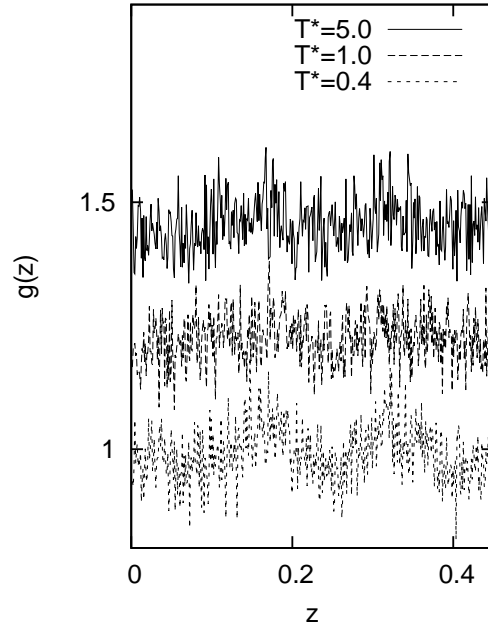


Figure 12: Density projection with respect to the director $g(z)$ for $\sigma_x : \sigma_y : \sigma_z = 1 : 2 : 4.5$

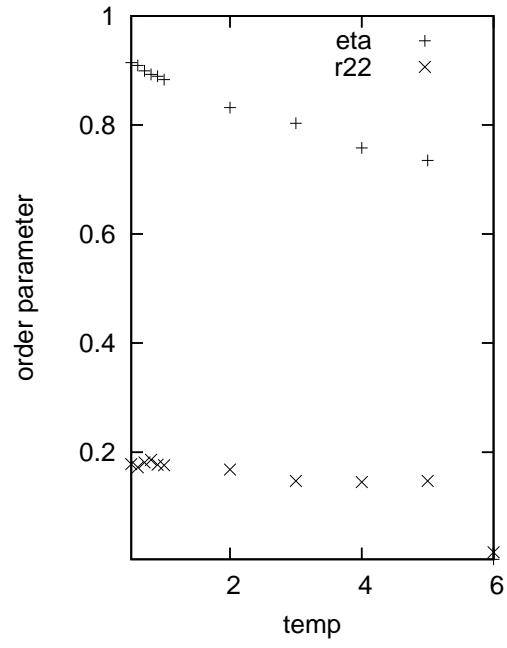


Figure 13: order parameters for $\sigma_x : \sigma_y : \sigma_z = 1 : 1.5 : 4.5$

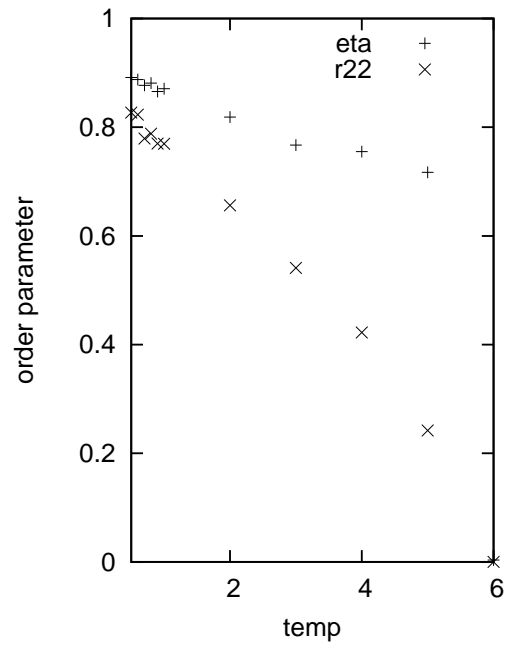


Figure 14: order parameters for $\sigma_x : \sigma_y : \sigma_z = 1 : 2 : 4.5$